

UCRL- 92857
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ISOTOPIC RATIO MEASUREMENTS WITH ICP-MS

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June 3, 1986

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This paper was presented at the 1986
Winter Conference on Plasma Spectrochemistry,
Jan. 1986, Kailua-Kona, Hawaii and submitted
for publication in Spectrochimica Acta, Part B,
Volume 42 (1/2) 1987.

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Presented

1986 Winter Conference on Plasma Spectrochemistry

January 1986

Kailua-Kona, Hawaii

Submitted for publication in

Spectrochimica Acta, Part B,

Volume 42 (1/2) 1987

ABSTRACT

An inductively-coupled-plasma source mass spectrometer (ICP-MS) has been used to measure the isotopic composition of U, Pb, Os, and B standards. Particular emphasis has been placed on uranium because of its nuclear and environmental interest and because of the availability of a well-characterized set of standards with a wide range of isotopic compositions. The precision and accuracy obtainable in isotope ratio measurements by ICP-MS depend on many factors including background, interferences, dead time, mass fractionation (bias), abundance sensitivity, and counting statistics. Which, if any, of these factors controls accuracy and precision depends on the type of sample being analysed and the characteristics of the mass spectrometer. These issues are discussed in detail.

Using a standard commercial instrument (Plasmaquad, VG Isotopes), uranium and lead sensitivities were $\sim 1 \times 10^6$ cps/ppm when the resolution was set to $< 10^{-4}$ overlap between adjacent peaks. After correction for dead time, background, and fractionation by software routines described herein, the $^{238}\text{U}/^{235}\text{U}$ ratios for < 1 ppm solutions agreed with the standard values within 0.5% for ratios ranging from unity to 200. For the minor U isotopes 234 and 236 agreement was within $\sim 10\%$ for abundances as low as 2×10^{-5} . For lead, NBS 981, the $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{204}\text{Pb}/^{206}\text{Pb}$ agreed with the standard values within 0.3% and had precisions of $\sim 0.3\%$. In all cases less than 15 ml of solution were consumed. Mass dependent

variations of the observed ratios (fractionation) from the standard ratios were observed in all analyses. These variations, which increased linearly with increasing mass difference, always favored the loss of the lighter isotopes from the measured beam. They are stable in magnitude for a period of hours and insensitive to operating parameters. Longer term variations were observed which also do not seem to correlate with the operating parameters. These effects, 1-2 %/amu, are distinct from the much larger instrument dependent effects reported by others. In contrast to other reports, no variation in boron (1 ppm) isotopic ratios was observed between a solution containing 40 ppm lead and a lead free solution. For Os, tetroxide vapor was introduced directly into the torch without the use of a nebulizer. This technique gave a factor of ~80 enhancement in signal over that obtained by nebulization and made it possible to measure isotope ratios to better than 1% precision for less than 5 ng of osmium.

1. INTRODUCTION

The ability to measure isotopic ratios is of considerable interest in a wide variety of research and measurement fields. This interest can in general be divided into the desire to make two broad classes of measurements. These are (1) variations in isotopic composition occurring in nature (natural or anthropogenic) and (2) isotope dilution studies to determine concentrations, volumes, and exchanges. For the metallic elements, the most commonly used instrumentation for such determinations is thermal ionization mass spectrometry (TIMS). For isotope ratio measurements on the alkali, alkaline earth, lanthanide, and actinide elements, TIMS is an exceedingly powerful technique. Using commercially available equipment, it is possible to measure isotope ratios more precisely than one part in one-hundred-thousand for ratios near unity, while operating with an abundance sensitivity of $\geq 500,000$, a dynamic range of the detector of $\geq 1,000,000$, and consuming a few ng of the element of interest. The technique however has several significant drawbacks. Analyses typically require hours of instrument time after days of sample preparation time, and the technique is limited to the more easily ionizable elements. It also can not be used for concentration work except for isotope dilution determinations. Other techniques; e.g., spark source mass spectrometry, have different but no less severe problems. It is therefore of interest to evaluate inductively-coupled-plasma source mass spectrometry (ICP-MS) as a possible way to simplify analyses and extend the number of elements which can be analyzed without highly specialized techniques.

The purpose of this investigation was to evaluate how well ICP-MS could be used to determine isotope ratios and to identify the factors which limit its use. Among the factors investigated were background, abundance sensitivity, sensitivity, dead time, mass fractionation, isobaric interferences, operating conditions, and matrix effects. Because this was a performance evaluation, no attempt was made to analyze anything other than standards.

Although this paper is restricted to standards, it is important that the reader have an understanding of where isotopic variations exist in nature and some feeling for the magnitude of such effects. All known isotopic variations can be grouped into five classes. The most common cause of variations is mass fractionation which has been extensively exploited with the light elements and is the basis of so-called stable isotope mass spectrometry. Mass fractionation is also observed as an instrumental effect which tends to obscure naturally occurring fractionation, particularly above mass ~40. The magnitude of these naturally occurring fractionations is generally less than 1% per mass unit and frequently less than 0.1% even among the lighter elements where the fractional differences in the masses of isotopes are large. Measurement of such effects depends on the ability to control the instrumental component of fractionation (~1% per amu in ICP-MS) and to reference measurements to standards. The second type of variation is changes in isotopic composition due to the ingrowth of radioactive decay products. With the exception of the lead isotopes, such variations tend to be <1%, but larger variations are possible and depend on the parent daughter ratio. In determining these variations, it is necessary to first correct the data for mass

[fractionation. This is normally done by assuming a functional form for the mass dependence of the fractionation and normalizing to a constant value for a ratio not affected by decay. Having made the fractionation correction, it is frequently possible by TIMS to measure isotopic shifts due to radioactive decay to precisions of a few parts in 10^5 . The next two types of isotopic shifts are those due to cosmic ray effects and primordial variations. These effects are generally restricted to extra-terrestrial materials and tend to be small; i.e., $<0.1\%$. The last class of variation is that due to isotope separation and the nuclear industry. Isotope dilution studies can be included in this category. Obviously the magnitude of anthropomorphic effects is highly variable, but the number of elements with widely disseminated effects is small.

In summary except for the lightest elements, it is highly unlikely that one would be able to use ICP-MS to identify variations in isotope ratios due to natural fractionation because the instrumental fractionation is expected to be substantially higher than the known range of natural variation. On the other hand, it will be shown that ICP-MS holds considerable promise for measuring other types of isotopic variations in those cases where the variations are at least a few tenths of a percent in magnitude.

To evaluate the performance of the Plasmaquad, a series of uranium isotopic standards were used. Uranium was selected as the principle element of study because uranium isotopic analyses are of interest in the nuclear industry, environmental monitoring, and for geochemical problems, and because there exists a widely available set of isotopic standards prepared by the U. S. National Bureau of

Standards (NBS). These standards cover a wide range of isotopic composition for both $^{235}\text{U}/^{238}\text{U}$ and the minor isotopes ^{234}U and ^{236}U . Uranium analyses were used to evaluate sensitivity, abundance sensitivity, resolution, deadtime, methods of peak integration, and dynamic range. Because of the potential importance of ICP-MS to lead isotopic analysis in the geochemical community, an NBS lead standard (SRM 981) was analyzed to show the instruments capability. In light of reports (1) of matrix effects altering the measured isotopic composition of light elements, a boron standard was analyzed in the presence and absence of lead. A summary of the osmium isotopic analyses (2) done in conjunction with A. R. Date of the British Geologic Survey on his prototype instrument (3) is presented to show the potential importance of signal enhancement techniques and the linearity of the mass fractionation.

2. INSTRUMENTATION

A Plasmaquad ICP-MS manufactured by VG Isotopes was used for the work presented here except for the Os analyses. Except as noted the instrument was used as standardly supplied. In order to evaluate background and high count rate performance, three types of multipliers were used. Two were of the continuous dynode type (DeTech and Galileo). The third was a developmental unit of the discrete dynode type (ETP). For the discrete dynode multiplier, the potential of the front plate was adjusted independently of the dynode string voltage. In order to reduce rf noise from the quadrupole and torch power supplies additional screening was added at various locations. Foreline traps were added to the mechanical pumps of the vacuum system to protect against mechanical pump oil backstreaming into the system. Sampling apertures, the orifice allowing plasma to enter the spectrometer, were made of TiN coated Ni supplied by VG Isotopes. The central channel diameter as supplied was 0.75 mm, but was allowed to erode to 1.1 mm before replacement. The work reported here was with an aperture having a ~1.0 mm opening. Sample was aspirated at a rate of ~1 ml/min. No sample pumping was used. All solutions were prepared in 2% HNO₃ and were generally at concentrations ≤1 ppm. Although the instrument is supplied with a mass flow controller on the nebulizer gas supply, it was disconnected during the work reported here.

Pulses from the electron multiplier were directed to an amplifier, lower level discriminator. Output pulses from the discriminator are sent to a multichannel analyzer (MCA) operated in the multichannel scaling mode. The dwell time per channel in the MCA was controlled by a microprocessor which also controls the mass scan of the quadrupole. All data reported here were taken in a scanning mode, but peak-jumping is also possible. The mass range to be scanned could be as wide as 300 mass units or as narrow as five mass units, and selected mass regions within a scan could be scanned more rapidly than the rest providing what amounts to skipped regions. Spectra can consist of 512, 1024, or 2048 channels with dwell times from 10 microsec. to 65 millisec. per channel. In the skipped regions, the system is swept at 15 microsec. per channel. Normally data are acquired at a sweep rate of one to ten scans per second, and one to two minutes of scans are summed in the MCA before the accumulated data are transferred to the computer (IBM-XT). The maximum rate at which data can be collected depends on the characteristics of the multiplier, the width of the discriminator output pulse, and the minimum pulse width acceptable by the MCA. The characteristics of the various multipliers used are discussed below. As supplied the discriminator pulse width was 70 ns, and this was the minimum time between sequential pulses without loss for this work. Subsequently the discriminator output width was reduced to 50 ns. which is near the limit for acceptance by the MCA. Further reductions in pulse width and hence deadtime would require abandonment of the MCA method of data collection and the use of peakjumping. As discussed below (Section 3.6), this does not imply that the MCA approach is not a good one.

3. DATA REDUCTION

3.1 General

In order to properly interpret the data collected with any instrument one must evaluate the operational performance of that instrument and the techniques of data reduction. In this section we will attempt to address these issues.

3.2 Resolution and abundance sensitivity

Among the most important parameters characterizing the performance of any spectrometer, are its resolution and sensitivity. Throughout this work, the instrument was operated with near baseline resolution between adjacent masses. Figure 1 shows the sum of twelve typical to slightly poorly resolved uranium spectra each of which resulted from a one minute accumulation from a 0.5 ppm solution of UO05. In this spectrum the full width of the ^{238}U peak at the baseline is ~ 1.1 amu. The valley between two adjacent peaks of equal intensity would have been $\sim 0.2\%$ of the peak top intensity if such peaks had been present. Using a 5% valley definition, the resolution, $M/\Delta M$, is 1.2M for the composite spectrum. Obviously the resolution was somewhat higher for the individual spectra used to calculate the isotope ratios.

If one defines abundance sensitivity; i.e., the tailing of one mass into adjacent masses, as the ratio of the areas under the peak at mass 238 to the area at mass 237, then the abundance sensitivity is ~ 2000 if the areas are each calculated for a full mass unit width and background is subtracted. If one uses 0.8 amu, the width

normally used in the data analysis, as the width over which the areas are calculated, the abundance sensitivity would be $\sim 80,000$ after correcting for background using the average of the counts at masses 233, 240, and 241. In that there is no obvious tailing of the 238 peak into the mass 237 region, the actual abundance sensitivity may be considerably higher and the excess counts at 237 may be due to a small, unidentified interference peak. The small bump at mass 237.1 is a precursor peak associated with mass 238. This bump amounts to $< 1 \times 10^{-5}$ of the 238 and half of the excess counts at mass 237. While this is a small effect, such precursors can seriously reduce abundance sensitivity and effect the measurement of minor peaks.

Figure 2 shows a lead spectrum collected under the conditions used for some of the uranium data reported here, but slightly different from those used to obtain Figure 1. The peaks in this spectrum are clearly baseline resolved. Such spectra were obtained while maintaining good sensitivity. This makes it unnecessary to operate in a low resolution mode.

3.3 Sensitivity and background

The sensitivity of the instrument depends in part on the performance of the electron multiplier, but a meaningful evaluation of sensitivity must also include a discussion of background because the "figure of merit" of the system depends on both parameters. For low intensity peaks, the figure of merit of the system will increase roughly as S^2/B where S is the signal due to the sample and B is the background (4). For high intensity signals ($S \gg B$), the figure of merit improves as the square root of the intensity.

The performance of the continuous dynode type multipliers differs from that of the discrete dynode multiplier in several important ways. Unfortunately all of these differences do not favor the same system. The pulse height; i.e., energy, distribution of the continuous dynode system is such that pulses due to ions are well resolved from those due to low energy continuum noise. It is therefore possible to set the discriminator above the noise pulses without significantly cutting into the distribution of ion generated pulses. This means that one can obtain a relatively flat plateau of count rate versus dynode voltage. For the discrete dynode multiplier used, the count rate continues to increase with dynode voltage. The settings of the discriminator and high voltage were selected by varying both parameters until the optimal figure of merit was achieved.

A total of three continuous dynode multipliers (one from Galileo and two from DeTech) were used. These had similar properties in that all gave backgrounds of 30-100 c/s and sensitivities for uranium of $(1-3) \times 10^6$ c/s per ppm when on a peak top.

For the discrete dynode multiplier, the sensitivity for uranium could be varied widely because of the lack of a plateau, but reasonable sensitivities were only obtained when a voltage was applied to the front plate. To apply this potential, it was necessary to isolate the plate from the first dynode to which it is normally shorted. The optimum front plate voltage was found to be ~ 160 v negative with respect to ground. The dynode voltage was also negative with the anode at ground. At a sensitivity of 2×10^6 c/s per ppm for uranium, the background was ~ 120 c/s. When the sensitivity was

lowered to 1×10^8 c/s per ppm by adjusting the multiplier voltage and discriminator settings, the background was reduced a factor of four to ~ 30 c/s. Although these settings correspond to similar figures of merit for small signals, the lower sensitivity case was chosen for the work reported here even though the performance for large signals would not be predicted to be as good. It was felt that the uncertainty on the background might not be controlled only by Poisson statistics and should be minimized. The lower sensitivity also leads to less significant dead time corrections.

A much lower background of 4 c/s with only a 40% decrease in sensitivity; i.e., a factor of 2.6 improvement in S^2/B was subsequently found while using a smaller diameter aperture (0.75 mm). To test whether this change was due to the aperture or to the multiplier, the larger aperture was put back on the system. It gave an intermediate sensitivity but essentially the same S^2/B as the original work. It appears that in the time interval of two months between the two sets of measurements, the sensitivity decreased somewhat either due to changes in operating conditions or multiplier aging. The improvement in S^2/B appears to be due to the aperture and not to aging of the multiplier. In that this multiplier was specifically designed to be insensitive to photons, such behavior would not have been predicted. It is not clear whether the size of the aperture or some other effect such as surface finish (5) caused the changes in S^2/B . Further work will be required to discern what is controlling the background and how best to operate the system.

Although it has no obvious effect on the data reported here, it should be noted that a 360 Hz ripple was observed on the ion beam signal. This ripple which amounts to 20-30 % of the beam intensity appears to be associated with the full wave rectified three phase power used for the plasma torch. This instability could be significant in rapid single pass data collection or possibly peak jumping if short integrations were used or if mass scans were triggered by line frequency.

3.4 Interferences

Isobaric interferences can arise from many causes including nuclear isobars, doubly charged ions, hydrides, oxides, and other molecular peaks. For uranium the level of doubly charged, oxide, and hydride ions relative to U^+ were 1-2%, 3-5%, and $\sim 1 \times 10^{-4}$ respectively. For barium the doubly charged and oxide peaks were $\sim 3 \times 10^{-3}$ and 1×10^{-3} . These are typical values and no attempt was made to minimize them. In addition Hg ions were observed in the Pb spectra which required a correction to the ^{204}Pb data.

3.5 Peak integration and background subtraction

All data were initially reduced with the software routines supplied with the instrument. For peaks with greater than some threshold number of counts, these programs calculate the areas of the peaks by summing all the channels between count rate minima on each side of a peak. For small peaks, the channels within a fixed mass range are summed. Backgrounds are subtracted by running a "blank" and subtracting the blank spectrum from the sample spectrum. The blank

may in fact be the average of several data accumulations. This approach to data reduction worked for peaks which were large relative to the background and threshold, but for smaller peaks, two problems were encountered. First the number of channels included in the calculation of the background to be subtracted from a peak was not in general the same as the number included in the peak itself. This led to an incorrect determination of the net counts in the peak. The second problem was that for masses where no peak should have been present the background corrected net counts did not average to zero.

To overcome the first problem, which in this work was significant only for the minor isotopes of uranium (234, 236, and for U005 only 235), the raw data were reintegrated using a fixed interval of 0.8 amu per peak. To do this it was necessary to recalibrate the mass scales associated with the spectra to ensure that the peaks were indeed centered in the integration windows. Fortunately the mass calibration was quite stable over a series of runs so that a single calibration could be applied to a whole series of runs. Within a given day's data, run to run variations in mass calibration were observed only once and only within the first few accumulations. In this case the variation was in the form of a slight shift in the entire spectrum rather than a shift in separation between peaks. For this reason, accurate ratios could be determined even without individually recalibrating those spectra. The reintegrated peak integrals were then transferred to a Symphony (Lotus Development Corp.) spreadsheet for further analysis (6).

The proper correction for background is complicated by the presence of at least four separate components. These are the continuum background due to photons, shot noise, and the like, memory from previous samples, reagent blank, and isobaric interferences (atomic and/or molecular). Isobaric interferences must be subtracted on the basis of known ratios of peaks due to the interferant. In this work, isobaric interferences were observed as ^{204}Hg on ^{204}Pb and ^{235}UH on ^{238}U . Memory and reagent blank are best removed by subtracting separately accumulated spectra for solutions devoid of sample. This is the method used in the standard VG software. It was found to be the most appropriate correction when sample to sample variations in concentration were large and accentuated memory. The blank spectrum subtraction method would be expected to be appropriate for minor isotopes, but this was found not to be the case. In uranium spectra, the blank subtracted peaks calculated using the fixed peak width method at masses 233, 240, and 241 were found to be similar and non-zero. This was interpreted as being due to a shift in the continuum background between the blanks and the samples. The uranium spectra were therefore background corrected by subtracting the average value of the 233, 240, and 241 masses from the uranium peaks. As shown below this gave a substantial improvement in accuracy and precision for the measurement of the minor isotopes 234 and 236 which were present at levels as low as 2×10^{-5} of the 238 or 0.01 ppb! Masses 237 and 239 were excluded from the background calculation because of the slight excess count rate at 237 and the presence of UH^+ at 239. The ^{238}U data were corrected for ^{235}UH on the basis of the observed 238/239. For a series of analyses of a given

sample, typically 10-12 one min. accumulations, somewhat better precision was obtained by subtracting the average background for the accumulations from each of the individual spectra rather than the background specific to that accumulation. Therefore, average backgrounds were subtracted.

3.6 Dead time

At high count rates, two effects come into play which cause pulse counting systems to count less events than actually occur. The first of these is the loss of counts due to the finite time after an event during which the system is incapable of recording another event. This is the time necessary for the system to electronically process the event and reset itself in preparation for the next event. The mathematical form of this effect, usually called dead time, τ , depends on the details of the system and can be of the "paralysable" or "nonparalysable" type (7). If the true rate, n , is much less than $1/\tau$, then for either case

$$m \approx n(1 - n\tau)$$

where m is the observed rate.

The second effect is a loss of gain at high count rates caused by the inability of the multiplier's dynode string to supply enough current to maintain constant dynode voltage drops. As the gain drops, an increasing fraction of the pulses are of insufficient amplitude to trigger the discriminator and thus be recorded. This effect, often called sag, is evidenced by a sharp increase in apparent dead time at high count rates.

Although the continuous dynode multipliers have good operating plateaus in terms of counts verses dynode potential, the low current capacity of the dynode coating means that sagging is a serious limitation at high count rates. When using the continuous dynode multipliers, the instrument was extremely sensitive (3×10^6 c/s per ppm U). Even for half ppm solutions, the most dilute employed, the observed isotope ratios were systematically biased in favor of the less abundant isotopes. This was originally interpreted as a dead time effect of ~ 200 ns (8). As pointed out by Boorn et al (9), this is more likely sagging of the multiplier, and the apparent 200 ns dead time correction applies only at that particular count rate range. At lower rates a smaller correction should apply, but we have not made such measurements.

The situation is quite different with the discrete dynode multiplier. As shown in Figure 3, which displays the $^{238}\text{U}/^{235}\text{U}$ data for the U005 standard as a function of count rate, the isotopic ratios diverge linearly from the NBS values with increasing count rate as would be expected for dead time. The linear variation of ratios with count rate shows that this system is responding to dead time not sag up to a rate of at least 2×10^6 c/s as measured at the peak top. The point at 3×10^6 c/s falls about one percent below the trend of the other data and may indicate that sag is starting to come into play. The specifications for the multiplier claim 10^8 c/s as the upper end of its range, but higher rates have not been tested.

The dead time correction needed to make the ratio independent of rate and to bring it into agreement with the standard value was 70 ns where the correction is applied on a channel by channel basis to the

raw spectrum. An examination of the pulse widths within the system showed that this dead time was due to the output width of the discriminator. Subsequently this width was reduced to 50 ns with no adverse effect. Further reduction of the dead time is impractical with the existing multichannel analyzer because it requires an input pulse width of at least 45 ns. To obtain lower dead times, one would need to adopt a peak jumping strategy and a fast scaler. Such modifications are possible with the existing system if one is prepared to add the scaler, but it is not clear that such a change would be well advised. It would certainly not make sense with a continuous dynode system, and even with the fastest systems, the dead time could not be reduced much below 10 ns.

3.7 Mass fractionation

The observed isotope ratios also show a deviation from the standard values which is a function of the difference between the masses of the two isotopes being ratioed. Figure 4 shows Os results illustrating such deviations. This effect which is often the composite of several different effects following indistinguishable mathematical functions is variously referred to as fractionation, bias, and discrimination, and attempts are often made to separate these into separate effects. Sometimes this is possible as in thermal ionization mass spectrometry where the bias of an electron multiplier relative to a Faraday collector can be distinguished from the Rayleigh fractionation of the sample as it is evaporated from the filament. In some ICP-MS cases such as those reported for some Sciex systems (e.g. 10), the discrimination is clearly an instrumental

effect due to the transmission of the ion optics. In that the effects observed in this work, are stable over hours, are not obviously correlated with operating parameters, and are always in the direction of loss of the lighter isotopes from the beam, we have chosen to label the effect mass fractionation even though it is not clear whether it is a sampling or transmission effect. One should note that in ICP-MS the manifestation of fractionation is different from thermal ionization because the sample is continuously flowed through the sampling system rather than loaded as a batch. The fractionation therefore does not vary during a run. The effect observed here also differs from that reported for the Sciex instruments in that in those units the ratios deviate on both sides of the expected ratio.

For all of the samples measured, the deviation of the measured ratios from the true ratios is a linear function of mass to the precision of the data. This is illustrated for the osmium case by Figure 4 which shows the fractionation in a single 5 ng sample. It is therefore possible to relate the true ratio of isotopes A and B, $(A/B)_t$, to the measured ratio, $(A/B)_m$ by the equation

$$(A/B)_m = (A/B)_t \times (1 + a \times n)$$

where a is the fractionation per mass unit and n is the mass difference between isotopes A and B. For those cases, such as Os, where there are at least two isotopes which do not vary in natural samples, it is possible and desirable to correct for fractionation within the sample by normalizing the data to a constant, accepted ratio of those isotopes. In those cases where there is no pair of isotopes which do not vary; e.g., Pb and U, one must run a standard to determine the fractionation and then run the sample and assume the same fractionation applies. For U the NBS standard U500 is preferred

because the $^{238}\text{U}/^{235}\text{U}$ ratio is essentially unity (1.00030) and the dead time correction cancels out. As shown in Table 1, the fractionation in uranium varied from day to day but was constant within experimental errors for a period of hours. For all of the analyses performed the fractionation was in the range of $\sim 1\text{--}2$ $\text{\%}/\text{amu}$ except for the very light elements Li and B where the effect was larger. Although percent per mass unit corrections are large, their constancy and linearity allows isotope ratios to be measured to precisions of a few parts per thousand, as will be shown below, even when internal fraction corrections can not be applied.

Obviously it is of interest to understand the origin of the mass fractionation within the system, to control it, and to minimize it. Following the idea that fractionation might be due to preferential loss of the lighter isotopes by gas scattering, measurements of the $^{238}\text{U}/^{235}\text{U}$ in U500 were made for a variety of gas flows, aperture diameters, and sample aperture to skimmer separations. (The skimmer is a cone which defines the end of the first vacuum stage and is the second element of the ion extraction system. It has a 1 mm diameter axial hole to allow passage of the ion beam from the first vacuum stage to the focusing lenses.) No significant variation in fractionation was observed.

The first lens element after the skimmer is the extraction lens. It was observed that the relative Li to U sensitivity could be varied as a function of this lens setting and that the optimal extraction lens potential varied as a function of the diameter of the hole in the sampling aperture. However varying the extraction potential had no effect on fractionation. Similar negative results were obtained when the energy of the ions entering the quadrupole was varied. In

that variations in fractionation are observed on a more or less daily basis and resolution is normally set daily, the observed fractionation may be controlled by resolution. This possibility has not yet been evaluated. The monotonic increase of fractionation with time shown in Table 1 appears to be coincidental in that subsequent work has shown no systematic effect. At this time the true cause of fractionation in the system is unknown. Further, more systematic work is planned.

4. RESULTS AND DISCUSSION

4.1 General

Except as noted, the results reported here were obtained with the continuous dynode multiplier. These data except for osmium were collected during a four day period and no data have been rejected because of poor quality.

4.2 Uranium

Five different uranium standards were analysed at concentrations ranging from 100 ppb to 5 ppm and isotope ratios ranging from unity to 2×10^{-5} . To help one appreciate the sequence and importance of the data reduction steps described in Section 3, some sample reductions are shown in Table 2. Each case shown is for the average of twelve data accumulations of one minute each. For the blank run, the only peaks observable above the continuum background are at masses 235 and 238. These peaks are due to torch memory rather than reagent blank. They are equivalent to the signal from a 0.5 ppb solution and are insignificant for this work except as noted below. They do however serve to show that the detection limit is well below 0.1 ppb.

The second sample shown is a 100 ppb solution of U500. One sees from the count rates that for this (and only this) sample the elevated blank contribution at 238 is significant. For 238 in this sample, the blank's 238 was subtracted rather than the average of the 233, 240, and 241 counts as described above. It is quite possible to detect peaks; e.g., 236, when the counts due to the peak are less than those due to background, but that it is critically important

that the integration of such small peaks be done with attention to detail. For U500 more than any other of the samples analysed, the interference of ^{235}UH on ^{238}U must be taken into account. Even though the correction is only one part in 10^4 of ^{235}U , it is 5% on ^{238}U . Isotope ratios were calculated for each data accumulation rather than the average count rates to minimize the effect of fluctuations in sensitivity which scatter repetitive readings of intensity more than ratios of intensities. No uncertainty has been assigned to individual ratios. A comparison of the fractionation corrected, interference subtracted ratios, normalized to the NBS values (F.C./NBS), to those obtained by the VG procedure shows factors of three to ten improvement for the methods described here.

The last sample featured in Table 2 is an analysis of U005 from a half ppm solution. From the intensity (count) data, one sees the effect of the dead time correction on 238 and again the significance of the background correction. While the dead time correction is relatively small for this sample, it was shown in Figure 3 that at high count rates this correction is very important. On the other hand, the background correction is crucial for the minor isotopes because the counts due to the sample constitute only a few percent of the total. The blank run before this series of runs gave an average 233, 240, 241 background of 189 counts per peak whereas the average for the sample runs was 215. The difference is as large as the 234 peak.

Based on summed spectra, it can be argued that the slight excess at mass 237 is "real" and is due, at least in part, to a 10^{-5} precursor associated with mass 238. The standard deviation of the mean of the twelve measurements of the 237 is 50% of the mean number

of net counts; therefore by a two sigma criterion, a signal to noise detection limit of 0.005 ppb can be claimed. As in the previous example, the final values for the isotope ratios all agree with the NBS values within 1% of the measurements. The accuracy and precision are also much better than obtained by the VG data reduction methods for the same data. It should be noted that the main source of difference in the 238/235 value between the two methods is due to the use of a fixed rather than variable integration window and not to the method of background subtraction.

The data for all the uranium standards analyzed are summarized in Table 3. The fractional deviations of these measurements, relative to 235, from the NBS values are shown in Figure 5 where the deviations have been plotted against the observed isotope ratio relative to 238 multiplied by the total number of 238 ions collected in the 12 accumulations for each sample. This allows one to present all the ratios on a single plot. The solid lines on the figure define the one sigma precision which would be expected if the uncertainty were controlled by counting statistics including the uncertainty on the background. At low count rates; i.e., for minor isotopes, the precision appears to be controlled by counting precision. At higher rates other factors dominate.

The number of standard deviations of the mean of the ratios which those average ratios deviate from the NBS values are plotted in Figure 6. Over a range of 100,000 in the number of ions observed, there is no noticeable trend in the accuracy of the data relative to its precision and the data appear to be normally distributed. There is however a slight bias toward positive values. As shown in Figure 7, where the distribution of ratios is plotted separately for the

various ratios, the $^{236}/^{235}$ measurements are systematically high by about one standard deviation and account for the positive bias observed in Figure 6. This excess does not correlate with sample, $^{236}/^{235}$, or count rate and remains unexplained. Three significantly deviant points appear in Figures 6 and 7. The most negative point is the sample with the highest count rate and may reflect the limitations of the multiplier or the dead time correction. The other two appear to be random variations. Otherwise the data seem exceedingly well behaved, particularly considering the wide range of ratios and count rates.

4.3 Uranium plus lithium

It is often of interest to simultaneously measure the isotopic composition of several elements separated in mass. In the usual operating mode the Plasmaquad scans a mass region at a constant rate per mass unit. This leads to a low duty cycle when one is only interested in widely separated peaks. To address this problem we are developing a peak jumping capability. In the interim it was decided to test the VG supplied routine which allows one to essentially jump over mass regions where data accumulation is not desired. In actuality the system is scanned rapidly through unwanted regions and more slowly through the desired regions. Because the multichannel analyzer's channels are incremented during the fast scan regions as well as the slow regions to maintain mass calibration, one is limited in the number of channels available per peak to the total number divided by the width of the entire mass range. For widely differing mass regions, this limits the resolution to <10 channels per peak rather than the fifty or so used for the other work reported here.

Furthermore, the spacing of the channels is linear in mass, but one amu is not an integer number of channels; therefore when there are only a few channels per peak, the channels are not spaced consistently over the peak area. To test how effective this method of data collection was, a mixture of lithium and uranium (U100) was isotopically analyzed in both the fixed rate and skip scan modes. It was found that the precision of the analyses increased by a factor of two to three for the skip scan mode due to the increased fraction of time spent on the peaks. However, because of the limited number of channels, the calculated ratios varied strongly with the choice of integration window. A change of one channel in the mass calibration was sufficient to change the apparent ratios well beyond the internal precision of the data. These results are presented in Table 4 for different methods of data reduction. For equivalent integration times, this method of data collection when applied to widely different mass ranges gives significantly poorer precision and accuracy than the narrow mass scans reported above .

In these analyses, the lithium signal was dominated by torch contamination from previous analyses. It is therefore impossible to assess the accuracy of the $^6\text{Li}/^7\text{Li}$. This effect does however serve to emphasize the importance of memory in ICP-MS. It is also worth noting that the number of Li ions observed was actually less in the sample which contained 1ppm each of Li and U than in the blank. Whether this is a suppression effect or not has not been tested.

4.4 Matrix effects on isotope ratios

There have been reports (1) that the measured isotopic composition of light elements was sensitive to both tuning conditions and the concentration of high atomic weight elements. To test for such effects in our system, the isotopic composition of lithium and boron were measured in two solutions. One contained 1 ppm each of Li and B. The other contained 1 ppm each of Li and B plus 40 ppm of Pb. As for the analyses reported above the Li signal was dominated by memory but that is not a problem in that only changes in ratios were being investigated. Both solutions were analyzed with the instrument optimized for maximum lead signal. We had planned to reoptimize on boron and repeat the measurements, but it was found that the same conditions gave maximum signals for boron and lead. The second set of measurements were therefore omitted. As shown in Table 5 the presence of 40 ppm (weight) of lead; i.e., an approximately equal molar concentration, had no effect on the boron or lithium ratios. The boron is severely fractionated (15%) relative to its certified isotopic composition in both case. This fractionation deserves further study.

4.5 Lead

Because of its importance in geologic and environmental work, the isotopic composition of the common lead standard NBS 981 was measured. The average ratios for ten one minute analyses of a 1 ppm solution are given in Table 6. Figure 2 is the spectrum of one of these analyses. If the deviation of the 208/206 ratio from the NBS value is attributed to fractionation, then the fractionation corrected 207/206 agrees with the NBS value to within 7×10^{-4} and has a precision of 1×10^{-3} . The 204 peak has an interference from

Hg, but after subtracting ^{204}Hg on the basis of the observed ^{202}Hg , the accuracy and precision of $^{204}\text{Pb}/^{208}\text{Pb}$ is also at the few parts per thousand level. The fractionation for lead is significantly different from that observed for uranium at the same time and under the same conditions; cf., Table 1 data for 12/18. This suggests that one should use interelement fractionation corrections as suggested by Longerich et al. (10) with great caution.

4.6 Osmium

As part of a project to measure the half-life of ^{187}Re by changes in the isotopic composition of osmium (11), it was necessary to develop a method to isotopically analyze nanogram quantities of osmium. Osmium is a particularly difficult element to analyze by mass spectrometry because of its chemical properties including a high ionization potential. ICP-MS offered a way to overcome the difficulties if its overall efficiency could be improved.

One of the limitations of solution nebulization is the poor efficiency of the sampling system. Only about one percent of the sample is delivered to the torch. To overcome the nebulizer's inefficiency, an osmium tetroxide vapor generation technique was developed which gave a factor of ~ 80 enhancement in signal over that obtained by nebulization or an overall efficiency of $\sim 1 \times 10^{-6}$ ions/atom. This technique has been described elsewhere (2, 12, 13). The average ratios of 12 analyses of a sample of natural osmium are given in Table 7. Each analysis was for a sample containing between one and five nanograms of osmium. The ratios obtained are in good agreement with those of Nier (14) and Luck and Allégre (15) and show precisions of a few parts per thousand for the

combined analyses. Precisions for individual analyses were controlled by counting statistics. The ^{184}Os was determined to better than five percent precision from a total of less than 10 pg of the isotope. Further improvements are expected due to increases in instrumental sensitivity and peak jumping, but these results serve to show that alternative sample introduction techniques can be used to improve the sensitivity of ICP-MS isotopic analyses.

5. CONCLUSIONS

It has been shown that ICP-MS can be applied to a number of problems involving the measurement of isotopic ratios. In order to properly interpret the data one must carefully and critically correct them for the effects of dead time, blank, memory, interferences, and fractionation. By switching from a continuous dynode electron multiplier to a discrete dynode type, it was possible to increase the dynamic range of the system by a factor of at least 2-3 and to reduce both the background signal and dead time. The dead time with the new system was dominated by the input requirements of the multichannel analyzer and can be set as low as 50 ns. Mass fractionation was found to be linear with mass within a given element and stable for a period of hours. This allows one to correct for fractionation, which occurs at the 1-2 %/amu level, even in elements where internal fractionation corrections can not be made due to a lack of isotopes occurring in a known ratio; e.g., Pb and U.

The ability to measure isotope ratios as small as 2×10^{-5} to the precision and accuracy limit of counting statistics has been demonstrated using the improved background subtraction and peak integration routines described. For ratios closer to unity than 200, precisions and accuracies of better than 0.5% were obtained. The measured isotopic composition of light elements in particular boron, while severely fractionated, was found to be insensitive to changes in the concentration of heavy elements (Pb).

The ability to simultaneously measure isotopic ratios for elements widely separated in mass is restricted by the existing system. The incorporation of peak jumping routines should solve this problem and allow one to integrate different masses for different

lengths of time. We are currently developing the software and hardware needed to do peak jumping in a way that allows the operator to select the number of scans to be accumulated, the masses to be measured, the number of points to be measured over a peak, the mass separation of those points, and the dwell time per point. In order for this scheme to be of optimal value, it will be necessary to move from point to point on a few milliseconds time scale.

As normally operated the efficiency of the system in terms of ions collected is $\sim 1 \times 10^{-6}$ if one monitors the peak top of a single mass. The effective efficiency when one scans a spectrum drops even further. For a ten mass scan, a factor of 20 is lost if one assumes triangular peaks. For many elements this is a much lower efficiency than can be obtained by other techniques; e.g., thermal ionization mass spectrometry. On the other hand, ICP-MS offers speed of analysis and the ability to measure additional elements; e.g., Os, which are difficult to analyze by other techniques. Even though the efficiency is low, based on the observation of the excess counts at mass 237, a two sigma detection limit of 0.005 ppb was observed in a series of scans which were ten masses wide and took 12 min. to accumulate. By using alternative sample introduction techniques, the relative abundance of ^{184}Os was determined to a precision of 5% in material containing less than 10 pg of that isotope. Further improvements can be anticipated.

ACKNOWLEDGEMENTS

We wish to thank Gerald F. Hunt for his unfailing support in maintaining and modifying the Plasmaquad hardware and software. We thank Dr. Alan Date of the British Geologic Survey, Dr. Alan Gray of the University of Surrey, and VG Isotopes for many helpful discussions on the subject of ICP-MS and for the use of their instruments in the early phases of our efforts to evaluate the potential of ICP-MS for isotope ratio measurements. This work was performed under the auspices of the US Department Of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

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TABLE 1
Isotopic Fractionation in Uranium

NBS-U500 238/235 = 1.00030

DATE	TIME	238/235 ⁽¹⁾	FRACTIONATION/AMU
9/17/85	15:45	1.0244 ± 10 ⁽²⁾	0.0081 ± 3
	16:00	1.0249 ± 10	0.0083 ± 3
12/18/85	15:30	1.0345 ± 12	0.0114 ± 4
	18:30	1.0304 ± 13	0.0100 ± 4
12/20/85	17:34	1.0535 ± 20	0.0177 ± 7
12/21/85	11:56	1.0571 ± 16	0.0189 ± 6
	14:30	1.0552 ± 16	0.0183 ± 6

- (1) Average of 10-12 runs of 1 min each. [U]_{sept} = 250 ppb.
[U]_{dec} = 100 ppb. Sept. peak areas by VG routine. Dec. areas by
method described here.
- (2) 1σ_m

TABLE 2

Uranium Data Reduction

	234	235	236	237	238	239	Bkgrd(1)
Background							
Counts(2)	246	265	248	239	1184	251	247
- Blank	-1	18	1	-8	937	5	±0
1σm(3)	± 6	± 4	± 4	± 4	± 19	± 4	± 3
U500							
Counts(4)	1337	106139	429	249	112714	256	245
- Blank	1092	105894	184	4	111530(5)	11	±0
1σm	± 6	± 457	± 6	± 5	± 457	± 6	± 3
M/235	0.01031	±1	0.00173	0.00004	1.0535	0.000010	
1σm	± 7		± 6	± 4	± 22	± 5	
- Hydride	0.01031	±1	0.00164		1.0535		
1σm	± 7		± 8		± 22		
Fract. Corr.	0.01053	±1	0.00161		±1.0003		
1σm	± 7		± 8				
F.C./NBS	1.0069	±1	1.058				
1σm	± 70		± 51				
VG/NBS	1.109	±1	1.10		1.0540(6)		
1σm	± 11		± 10		± 74		
U005							
Counts(0 ns)(7)	238	6025	277	224	1221645	276	215
Counts(70 ns)	238	6026	277	224	1245754	276	215
-Bkgrd.	23	5811	62	9	1245539	61	±0
1σm	±4	± 26	±6	±5	± 4829	±4	±2
M/235	0.00392	±1	0.0107		214.38		
1σm	± 67		± 10		± 94		
-Hydride	0.00392	±1	0.0106		214.38		
1σm	± 67		± 10		± 94		
Fract. Corr.	0.00399	±1	0.0104		203.55		
1σm	± 69		± 10		± 99		
F.C./NBS	0.895	±1	1.10		1.0014		
1σm	± 15		± 10		± 49		
VG/NBS	1.71	±1	1.14		0.9789		
1σm	± 49		± 35		± 52		

- (1) Bkgrd is the average of the 233, 240, and 241 intensities for the set of accumulations (12 in these examples). The set average background is subtracted from each intensity measurement individually.
- (2) Average number of counts per accumulation.
- (3) Uncertainties on counts and ratios were calculated from the distribution of observations. No uncertainty in the observation itself or the background has been included. It has been assumed that fluctuations in the background are reflected in the distribution of observations. Because of this, the uncertainty on the gross and net counts are the same.
- (4) A 70 ns dead time correction has been applied but it is insignificant for the U00 data.
- (5) For this entry only the background correction was based on the analysis of a blank rather than the value derived in (1).
- (6) Measured rather than normalized for fractionation.
- (7) Value in parentheses used to correct for dead time.

TABLE 3

Uranium Data Summary⁽¹⁾

=====						
Sample Date	Conc. 238's (ppm)	238's (10 ⁶)	238/235	234/235	236/235	

U500	NBS certified ratios		1.00030	0.010425	0.001519	
	12/18	0.1	2.2	≡1.00030	0.010486 ± 105	0.001453 ± 50
	12/18	0.1	1.7	≡1.00030	0.010391 ± 99	0.001590 ± 61
	12/20	0.1	1.3	≡1.00030	0.010497 ± 73	0.001608 ± 77
	12/21	0.1	2.3	≡1.00030	0.010695 ± 68	0.001521 ± 38
	12/21	0.1	2.5	≡1.00030	0.010438 ± 62	0.001554 ± 49
U200	NBS certified ratios		3.9779	0.006226	0.01057	
	12/18	0.8	25.2	3.9716 ± 49	0.006292 ± 28	0.010622 ± 43
U100	NBS certified ratios		8.8028	0.006634	0.003719	
	12/18	0.5	25.6	8.807 ± 11	0.006603 ± 58	0.003732 ± 45
	12/21	0.5	24.0	8.741 ± 21	0.006717 ± 48	0.003767 ± 41
	12/21	1.0	38.4	8.766 ± 26	0.006625 ± 41	0.003707 ± 27
U020	NBS certified ratios		48.054	0.00613	0.00810	
	12/18	1.0	26.9	48.180 ± 74	0.00592 ± 12	0.00803 ± 18
	12/20	1.0	20.1	47.938 ± 131	0.00623 ± 18	0.00826 ± 17
	12/21	1.0	37.8	48.028 ± 102	0.00606 ± 7	0.00811 ± 11
U005	NBS certified ratios		203.29	0.00445	0.00952	
	12/18	0.5	15.7	202.35 ± 97	0.00578 ± 68	0.00871 ± 61
	12/20	0.5	14.9	203.55 ± 99	0.00399 ± 69	0.01044 ± 98
	12/20	4.6	50.0	204.14 ± 94	0.00441 ± 23	0.01018 ± 38
	12/20	4.6	117.4	201.04 ± 56	0.00446 ± 16	0.00998 ± 19
	12/20	0.5	11.9	202.62 ± 95	0.00361 ± 91	0.00930 ± 115
	12/21	0.5	18.6	202.56 ± 1.03	0.00380 ± 71	0.00972 ± 62
	12/21	1.0	32.3	203.20 ± 86	0.00478 ± 28	0.01005 ± 32
	12/21	4.6	77.6	202.57 ± 97	0.00458 ± 19	0.00962 ± 14

(1) All values are the mean of 12 one minute accumulations. Uncertainties are 1σ of the 12 measurements. Data are normalized to the average fractionation observed in 238/235 for U500 measured on the same day and under the same conditions.

TABLE 4

Li - U Simultaneous Analysis ⁽¹⁾				
	6/7	238/235	234/235	236/235
Standard	?	8.8028	0.006634	0.003719
<u>VG Routine</u>				
Full mass scan	0.0798	9.20	0.0088	0.0057
10m	± 5	± 7	± 7	± 5
Skip scan	0.0766	9.29	0.0087	0.0057
10m	± 3	± 3	± 2	± 2
<u>Livermore Routine⁽²⁾</u>				
First Integration				
Full mass scan	0.0724	9.20	0.0063	0.0066
10m	± 4	± 6	± 5	± 6
Skip scan	0.0746	9.32	0.0062	0.0038
10m	± 2	± 2	± 2	± 1
Second Integration				
Full mass scan	0.0764	9.22	0.0065	0.0038
10m	± 4	± 6	± 6	± 5
Skip scan	0.0744	9.35	0.0060	0.0038
10m	± 2	± 2	± 2	± 1

- (1) Li and U concentrations were 1 ppm each. Each analysis is the average of 12 one minute accumulations. No fractionation corrections have been applied. A measured 238/235 = 9.30 would imply a fractionation of 1.9% per mass unit.
- (2) The two data reductions presented below differ only in that the mass calibration was shifted by one channel in the definition of the spectral mass calibration.

TABLE 5

Matrix Effects⁽¹⁾

Sample	$^{10}\text{B}/^{11}\text{B}$	$^6\text{Li}/^7\text{Li}$ ⁽²⁾
1 ppm Li + 1 ppm B	0.2117 ± 7(3)	0.0729 ± 2
1 ppm Li + 1 ppm B + 40 ppm Pb	0.2107 ± 5	0.0731 ± 2
NBS	0.2473	

- (1) Average ratios for 10 one minute analyses. Concentrations are in weight ppm.
 (2) The Li signal was dominated by memory.
 (3) Uncertainties are low of the measurements.

TABLE 6

Lead Isotopic Analyses⁽¹⁾

	208/206	207/206	204/206	Fract./amu
Standard ⁽²⁾	2.168	0.9146	0.05904	
Measured 1 σ m	≈ 2.168 ± 2	0.9140 ± 11	$0.05894^{(3)}$ ± 18	0.0069 ± 5
Meas./NBS 1 σ m	≈ 1	0.9993 ± 12	0.9884 ± 31	

{1} Average of 10 one minute accumulations. [Pb] = 1 ppm.

{2} NBS 981.

{3} After correction for ²⁰⁴Hg which accounted for ~2% of the observed signal at mass 204.

TABLE 7

Osmium Isotope Ratios⁽¹⁾

	190/192	189/192	188/192	187/192 ⁽²⁾	186/192	184/192
Meas. 1 σ m	0.6443 ⁽³⁾ ± 7	0.3955 ± 5	≈0.3244	0.03790 ⁽³⁾ ± 15	0.03842 ± 14	0.000474 ⁽⁴⁾ ± 20
Nier ⁽⁵⁾	0.644	0.394	0.324	0.0401	0.0387	0.00043
L + A ⁽⁶⁾ 1 σ m	0.6438 ± 2	0.3968 ± 1	≈0.3244	0.03687 ± 2	0.03907 ± 2	0.00058 ± 6

(1) Average of 12 analyses of 1-5 ng Os each.

(2) Natural variations expected due to ¹⁸⁷Re decay in nature.

(3) One analysis rejected (>2 σ dev.).

(4) Average of 11 analyses. Twelfth did not include mass 184 in the scan region.

(5) Reference (14).

(6) Luck and Allègre, reference (15).

FIGURE CAPTIONS

Figure 1

Summed mass spectrum of 12 one minute accumulations for a 0.5 ppm solution of NBS U005.

Figure 2

Mass spectrum accumulated in one minute for a 1 ppm solution of the NBS 981 Pb standard. Note the presence of Hg at mass 202 which indicates an interference at mass 204.

Figure 3

The effect of dead time on the isotope ratios measured with a discrete dynode multiplier (circles) is shown by the deviation of the measured $^{238}\text{U}/^{235}\text{U}$ from the NBS value with increasing count rate. The linear nature of the deviation shows that it is due to dead time rather than sag. A 70 ns dead time correction is seen to bring the measured points into good agreement with the standard value. For comparison one sample measured with a continuous dynode multiplier is shown. It requires a much larger correction. The uncertainty on the data points (10m) is equivalent to the size of the points.

Figure 4

The linear nature and magnitude of the mass fractionation observed in this work is illustrated by these Os data showing the deviation of measured isotope ratios from the generally accepted values as a function of the difference in mass between the ratioed isotopes. Uncertainties are 1 σ counting statistics.

Figure 5

The accuracy of the uranium isotope ratios relative to the NBS values is plotted as a function of the number of ions measured. Data for all the isotopes and standards measured have been combined except 238/235 for U500 which was used to determine the fractionation corrections. Ordinate values are relative to mass 235. The solid lines are the 1 σ uncertainties expected from counting statistics including the uncertainty in the background corrections.

Figure 6

The accuracy of the uranium isotope ratios in terms of the precision of the data is plotted on the same abscissa and data set are the same as in Figure 5. No trend in accuracy/precision is apparent as a function of beam intensity. The data are however biased slightly toward positive deviations.

Figure 7

The data of Figure 6 have been replotted as histograms of deviations from the NBS values in units of the precision of the measurements. The $^{236}/^{235}$ ratios show a positive bias of $\sim 1\sigma$ and account for the bias noted in Figure 6. No one standard seems to be biased relative to the others.

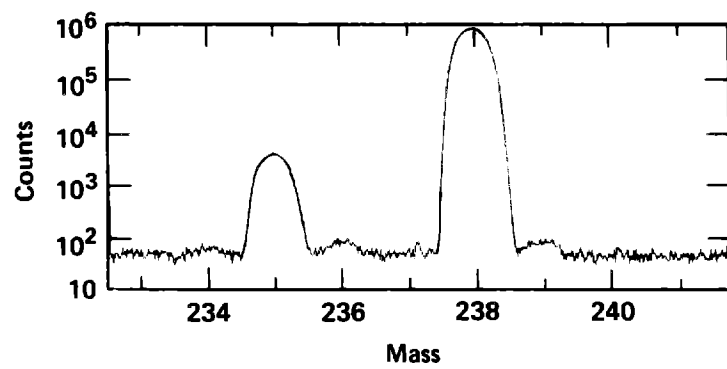


Fig. 1

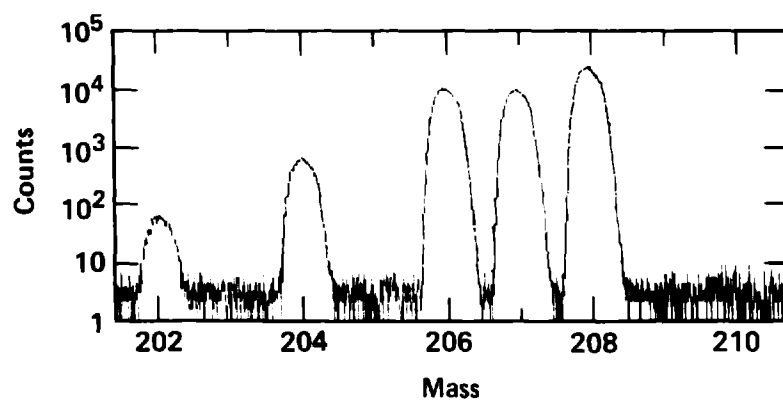


Fig. 2

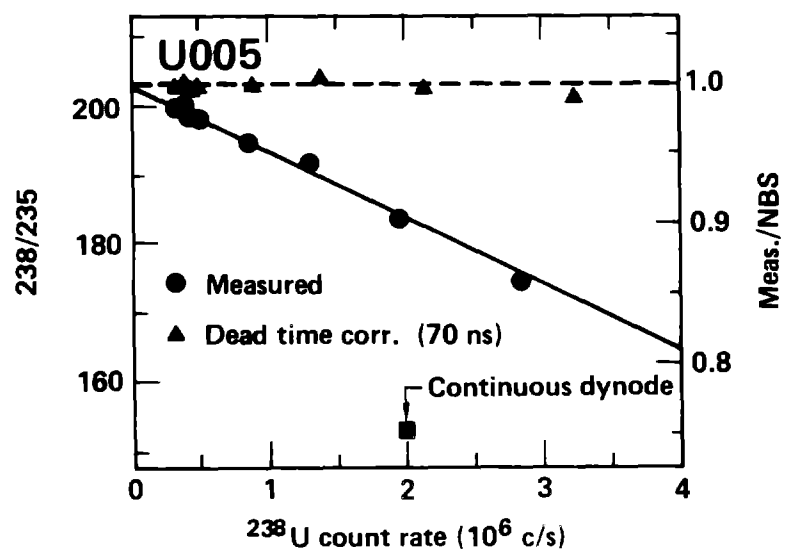


Fig. 3

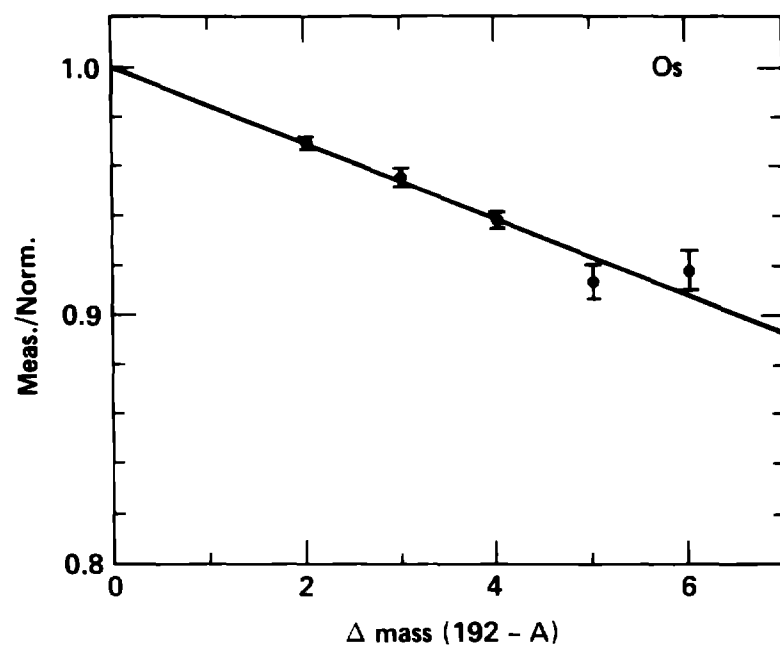


Fig. 4

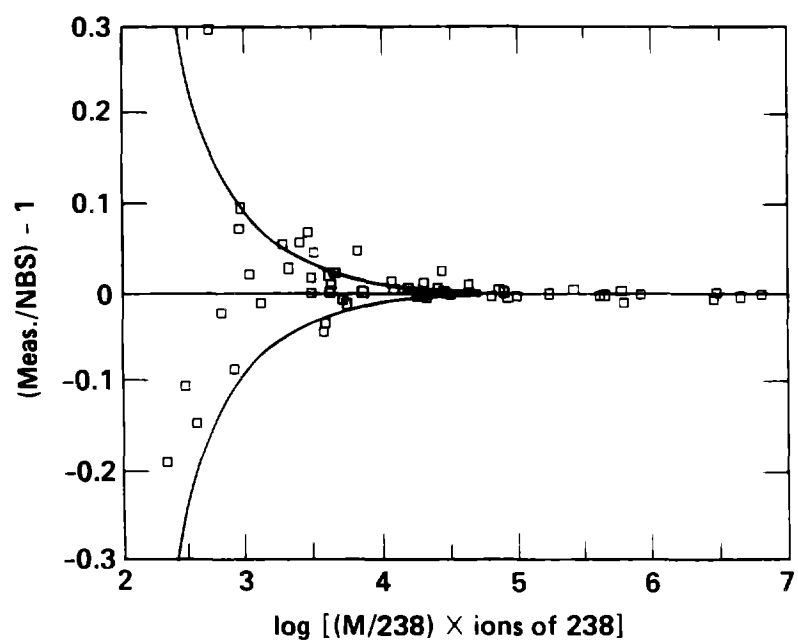


Fig. 5

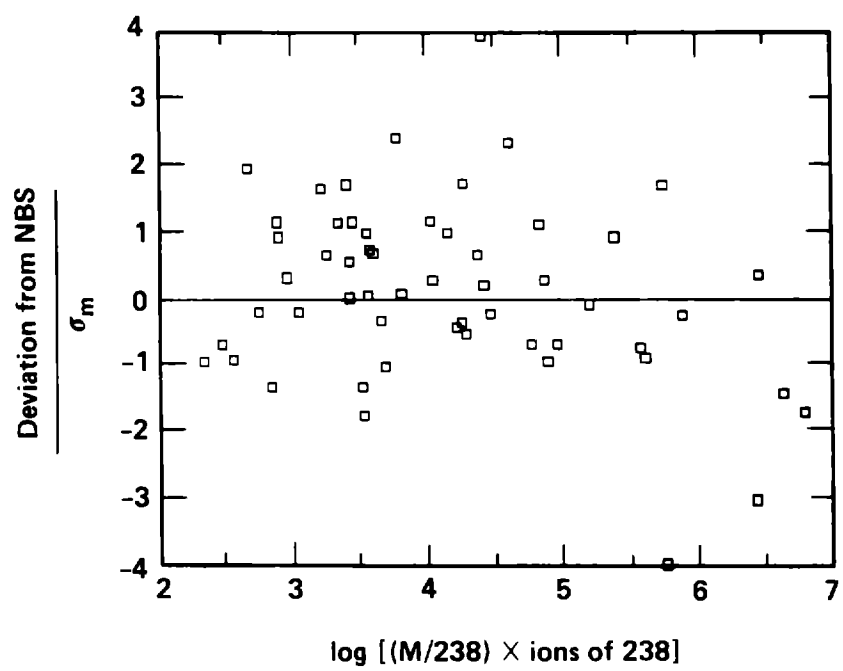


Fig. 6

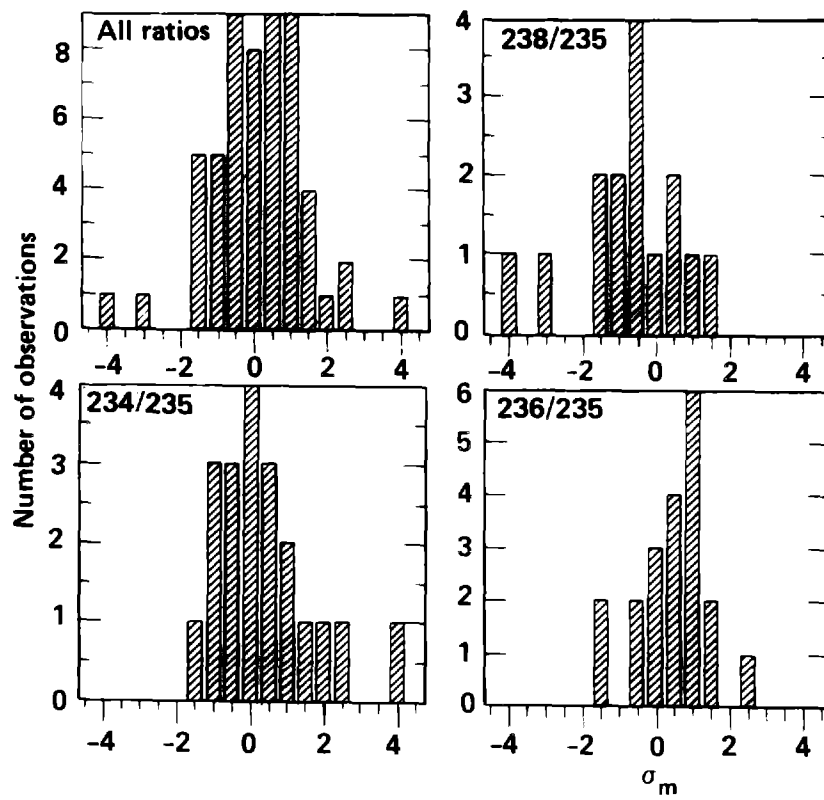


Fig. 7